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Dielectric and piezoelectric properties of $PbTiO_3$/PVDF and $BaTiO_3$/PVDF composites

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Abstract Synthesis of lead titanate ($PbTiO_3$) and barium titanate ($BaTiO_3$) based composites dispersed in a piezoelectric polymer (PVDF) have been undertaken. The composites were formed using sintered $PbTiO_3$ and $BaTiO_3$ powder dispersed in PVDF granules using dimethylformamide (DMF) as the solvent. Smooth (thick ~ 1 mm) films of $PbTiO_3$/PVDF and $BaTiO_3$/PVDF were made. The poled films were used for carrying out piezoelectric and dielectric measurements. The results indicate that the measured values of dielectric constant (ε') and piezoelectric charge constant (d_{33}) were strongly influenced by the relative proportions of the two constituents and the poling conditions.

Keywords Piezoelectric polymer, composites, dielectric properties

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1. Introduction

The rapid growth of polymer/ceramic composites has revolutionized many areas of science and technology because it has led to the discovery of many new engineering materials. The concepts of composites to be used in electronic devices have been neglected for many years. However, in the recent years the development of piezoelectric polymer/ceramic composites have opened new avenues for their applications in submarine, biomedical engineering, fishing industry, *etc*. Piezoelectric properties exhibited by some piezoelectric polymers and its composites made with ceramic are being exploited in a number of electromechanical transducer applications such as vibration and stress sensors, *etc*. This is because of their improved properties over the individual constituents in the composite systems with a continuous polymer medium and ceramic dispersoid. Such composite systems are easy to mold into various shapes. In addition, their properties can be tuned to our requirement by changing the proportions of the constituents.

During the last few years, many piezoelectric ceramic-polymer composites with different connectivity patterns have been fabricated [1-4]. Among them, 0-3 type of connectivity is one of the most commonly used configurations primarily due to its ease of fabrication coupled with its reasonably good properties. The lead zirconate titanate (PZT) based composites has assumed great significance because of the development of electrically active composites. The need for such composites arose because the conventional ceramic such as PZT is brittle in nature having poor acoustical matching and does not possess good hydrostatic response. Most of the work in this field, has been confined to the development of underwater acoustic hydrophones for low frequency range (< 40 kHz). Hydrophones made out of polymer/ceramic composites have remarkably higher values of sensitivity as compared to their ceramic counterparts.

A lot of work has been done on PZT/epoxy composites but not much has been reported on lead titanate ($PbTiO_3$) or barium titanate ($BaTiO_3$) based composites [5-7]. The present paper describes the structural, dielectric and piezoelectric properties of $PbTiO_3$/PVDF and $BaTiO_3$/PVDF composites.

2. Experiment

$PbTiO_3$ and $BaTiO_3$ were grounded with PVDF (Polysciences, Inc. USA) in required weight proportions. The composite mixture was dissolved in dimethylformamide (DMF) at room

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temperature. The slurry was homogenized and poured on to a glass substrate and heated in a dust free oven at 110°C for 2 hour to get a smooth translucent film (1 mm thick) of $PbTiO_3$/PVDF and $BaTiO_3$/PVDF composites. For dielectric and piezoelectric measurement the composite film was cut into circular pieces of 1.3 cm diameter and silver film was vacuum evaporated on both sides of these composites to make a Ag-composite-Ag structure. Dielectric measurements were done by a HP 4192A LF Impedance Analyzer. The test specimens were poled using high dc field at an elevated temperature. The piezoelectric parameter d_{33} was measured by using a Berlincourt's d_{33} meter.

3. Results and discussion

Figure 1 shows the measured values of dielectric constant at 1 kHz as a function of ceramic content for $PbTiO_3$/PVDF and $BaTiO_3$/PVDF composite at 300 K. The dielectric constants of both the composites could be controlled by adjusting the ratio of the constituents. The results can be explained by the relation proposed by Yamada *et al* [8] for the composite system, which is given as

$$\varepsilon_{comp} = \varepsilon_1\{1+[nq(\varepsilon_2-\varepsilon_1)/(n\varepsilon_1+(\varepsilon_2-\varepsilon_1)(1-q))]\}, \quad (1)$$

where n is the parameter attributed to the shape of the ellipsoidal particles, q is the volume fraction of the ellipsoidal particles, ε_1 is the permittivity of the continuous medium and ε_2 is the permittivity of the ellipsoidal particles. Taking the values of ε_1 = 10 for PVDF, ε_2 = 310 for $PbTiO_3$ and ε_2 = 1300 for $BaTiO_3$ and the value of n, chosen as 8 to fit eq. 1 ; the dielectric constant of the composites was calculated. The calculated values of dielectric constant at 1 kHz are in good agreement with the observed experimental values as can be seen from Figure 1.

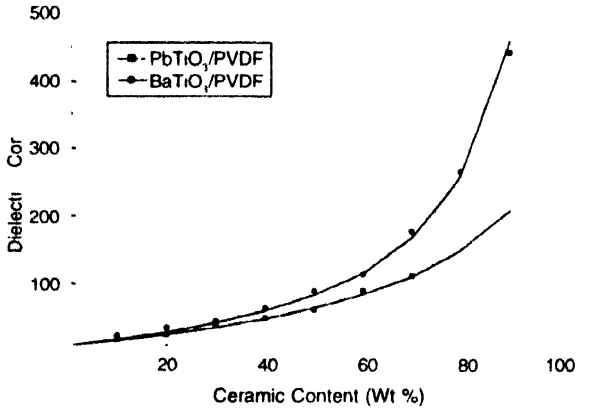

Figure 1. Variation of dielectric constant (ε') as a function of ceramic content measured at 1kHz and 300 K. The calculated values of dielectric constant using eq. (1) are shown by solid lines for both the composites.

Figure 2 shows the measured values of dielectric loss as a function of temperature in the range 0–130°C at 1 kHz frequency for 50/50 composites of $PbTiO_3$/PVDF and $BaTiO_3$/PVDF. It is evident from Figure 2 that ε'' increases with increase in temperature. However the increase is more in case of $PbTiO_3$/PVDF composite. The Curie temperature (T_c) of $PbTiO_3$ and $BaTiO_3$ are 490°C and 105°C respectively [1]. The glass transition temperature (Tg) of PVDF is ~ – 30°C. In the case of $BaTiO_3$/PVDF composite a relaxation in ε'' *versus* temperature spectra is observed in the temperature range 90-120°C, which may be due to the low T_c of $BaTiO_3$. In the case of $PbTiO_3$/PVDF composite, a relaxation is observed in the temperature range 40-60°C, which is attributed to the molecular motions of the crystalline regions of the polymer chain. This relaxation is not observed in $BaTiO_3$/PVDF composite. The high temperature relaxation of $PbTiO_3$/PVDF composite is not observed which may be due to high T_c of $PbTiO_3$. The high value of ε'' at high temperatures may effectively be due to ionic conductivity. The dielectric loss process is obviously related to the molecular nature of the polymer. The ceramic phase may provide added contributions of interfacial effects due to its presence in the amorphous phase of the polymer [9].

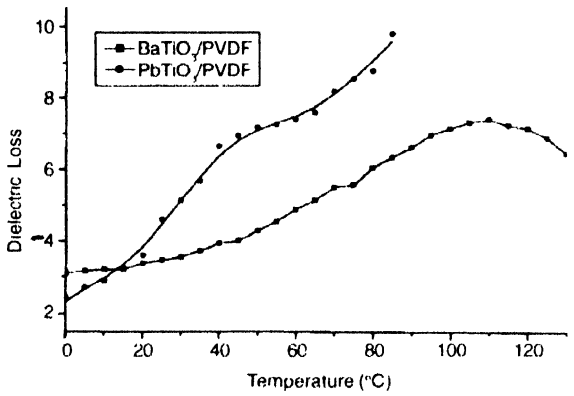

Figure 2. Variation of dielectric loss (ε'') as a function of temperature at 1 kHz for 50/50 ratio of both the composites.

The variation of d_{33} as a function of ceramic content for both the composites are shown in Figure 3. The value of d_{33} increases at a faster rate in the beginning and then slows down

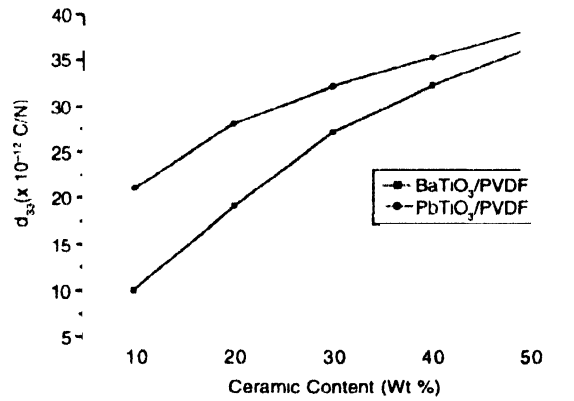

Figure 3. Variation of piezoelectric charge constant (d_{33}) as a function of ceramic content

at higher ceramic percentage in both the composites. The effect of poling field on d_{33} is shown in Figure 4. Both the composites were poles at 150 °C for 10 minutes. The fact that the d_{33} parameter is still increasing points out that the poling is still incomplete

This can be explained in terms of the fact that the field E_g acting on an isolated spherical particle is given by

$$E_g = E_0[3\varepsilon_1/(\varepsilon_2 + 2\varepsilon_1)], \quad (2)$$

where ε_2 and ε_1 are the dielectric constants of the spherical piezoelectric grains and the polymer matrix, E_0 is externally

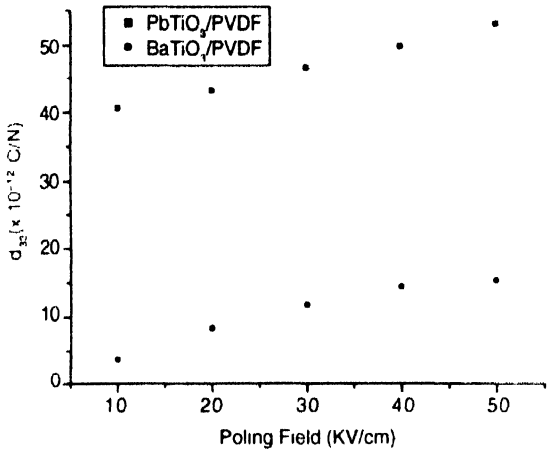

Figure 4. Variation of piezoelectric charge constant (d_{33}) as a function of poling field. Both the composites were poled at 150°C for 10 min.

applied field. For 0-3 composite of $PbTiO_3$/PVDF and $BaTiO_3$/PVDF, where $\varepsilon_2 = 310$ for $PbTiO_3$, $\varepsilon_2 = 1300$ for $BaTiO_3$ and ε_1 10 for PVDF, the electric field acting on the grain is very small. Typically for an applied field (E_0) of 50 KV, the actual field E_g acting on the grain is 1.13 KV in case of $BaTiO_3$/PVDF composite and 4.54 KV in case of $PbTiO_3$/PVDF composite, which are far too lower than the actual applied poling voltage. The calculated values of E_g (1.13 KV for $BaTiO_3$/PVDF and 4.54 KV for $PbTiO_3$/PVDF composites) are insufficient for carrying out the poling of the composites satisfactorily. Use of corona discharge to achieve better poling results has been suggested.

4. Conclusions

The dielectric behavior of the composites can be explained well by Yamada's relation [8], which furnishes a unique method to tailor these composites. The present study indicates that the effective field acting on the grain is a fraction of the actual applied field, which puts an upper limit on the d_{33} coefficient using conventional poling methods. This points out the fact that alternative technique such as corona poling should be adopted for getting better characteristics of these composites.

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